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by

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Langmuir-Blodgett films of aromatic Schiff's bases functionalized in the side chains of Polymethacrylate

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Synopsis

Langmuir-Blodgett (LB) film formation has been investigated for polymers in which nonlinear optical (NLO) moieties are attached in the side chain of polymethacrylate (PMA) backbone. Polymer monolayer was successfully transferred onto hydrophilic glass substrates using a moving wall type LB trough. The LB films were characterized by the pressure-area isotherm, polarized UV-visible spectra, ellipsometry and second harmonic generation measurement. The characterization shows that NLO moieties in the side chain are inclined to the plane of the substrate at a shallow angle. The second order nonlinear coefficient and molecular hyperpolarizability were also calculated.

INTRODUCTION

During the past decade, NLO properties of organic and polymeric materials have been extensively investigated¹. It has been established that the delocalized π -electron systems of acentric aromatic molecules can lead to higher second order NLO coefficients than those of traditional inorganic materials. A number of potential applications viz, second harmonic generation (SHG), frequency mixing, electro optic modulation have been proposed for materials based on these type of molecular structure. The material design of dipolar molecules with noncentrosymmetric structure and large molecular hyperpolarizability is a prerequisite for large second order optical effects. In addition, noncentrosymmetric alignment of the molecules on the macroscopic level is essential¹.

Recently, we have synthesized polymers in which the NLO moieties separated by flexible methylene spacer are covalently attached in the side chain of polymethacrylate (PMA) backbone². Aromatic Schiff's bases substituted with appropriate donor and acceptor groups have been chosen because of their large ground state dipole moment and large molecular hyperpolarizability³. We have also reported the NLO properties of these polymers that were spin coated and subsequently poled using a large electric field⁴.

The LB method is a convenient technique for producing very thin and uniform films that can be controlled to molecular dimensions. The close control of layer thickness and molecular orientation makes this technique particularly attractive for organization of NLO moieties. In this way, the alignment of NLO moieties can be achieved without the

poling procedure⁵. However, multilayer LB films usually have centrosymmetric alignment of molecules on the macroscopic level. Much effort has been invested to organize the material in a noncentrosymmetric film architecture^{6,7,8,9}.

In order to fabricate LB films which are thermally and mechanically stable over long periods of time, it is preferable to employ polymers rather than low molecular weight organic molecules. LB films prepared from polymers are expected to be stable and transfer onto a substrate without serious disruption in the oriented structure.

The polymers which we synthesized for this purpose possess an amphiphilic molecular structure. Hydrophobic polymer backbone with methylene spacer in the side chain also contain polar NLO moieties in the side chain. -CN and -NO₂ (polar groups) of NLO moieties are sufficiently polar to render them hydrophilic as well. Therefore the polymers are expected to form suitable LB films. There have been only a few research reports on nonlinear optical polymer LB films^{10,11,12,13}.

In this work the formation of LB films of candidate polymers and characterization of the NLO moieties' orientation in the LB film are reported. SHG measurement from LB films is used as a measure of nonlinearity and also molecular organization.

EXPERIMENTS

MATERIALS

Four different polymers were synthesized in our laboratory for the LB film growth. Polymer structures are shown in Fig.1. The synthesis procedure and polymer properties have been reported in an earlier communication².

PREPARATION OF LB FILMS

The LB equipment used in this work included both a conventional Lauda MGW film balance and a moving wall method LB film deposition apparatus (Nippon Laser & Electronics (NL-LB-240-MWC))^{14,15}. The moving wall apparatus consisted of a teflon trough, two teflon barriers (one fixed and the other movable) and teflon coated moving (side) walls. The width of the moving wall is the same as that of the substrate (50mm) to prevent shear flow of the monolayer during deposition. The moving wall is designed to move simultaneously with the moving barrier during compression and deposition to prevent friction between the monolayer edges and the wall. The surface pressure of monolayer is continuously monitored using the Wilhelmy plate method.

Polymers and stearic acid were dissolved in chloroform to a concentration of approximately 0.6 mg/ml and filtered through a 1 μm membrane PTFE filter and spread onto either pure water or $2 \times 10^{-4}\text{M}$ CdCl_2 subphase. The water was purified by distillation and passed through a Millipore Milli-Q system (Millipore Corp). A constant

temperature bath was used to control the subphase temperature. The glass slides and silicon wafers used for film deposition were cleaned by submerging them in a solution of NH₄OH, H₂O₂ and water (volume ratio 1: 1: 2.5) at 80°C for 20 min. They were then extensively rinsed with distilled water.

To measure the pressure-area isotherm, we used a constant strain rate compression (compression rate = 10% area/min). Compression speed gradually becomes slower as the surface pressure increases. In the high surface pressure region the monolayer is allowed enough time to relax to avoid collapse or squeezing. Monolayer films were transferred onto glass and silicon wafers. Glass substrate size was 70 x 50 mm. Most depositions were performed at a surface pressure of 15 mN/m. The dipping speed was 5 mm/min.

INSTRUMENTS

The UV-visible absorption spectra of LB films on the glass substrate were measured with a Perkin Elmer Lambda-9 UV-visible spectrophotometer. To examine the orientation of the NLO moieties in the LB films, the polarized absorption spectra were obtained with electric vectors oscillating parallel and perpendicular to the substrate. The angle of incidence for polarized light spectroscopy was 45°. The refractive index and thickness of LB films deposited on silicon wafers were measured with an ellipsometer (Rudolph Research). The incident beam wavelength was 633 nm and the incident angle was 70°.

Second order nonlinear optical coefficient (d_{33}), molecular hyperpolarizability and the orientation of NLO moieties (tilt angle) of LB

films have been measured by SHG measurement from 1064 nm laser radiation. These measurements were made with a Q-switched Nd-YAG laser (Quantel 660A). p- or s- polarized incident beam of 1064 nm wavelength was passed through the sample (LB film on the glass substrate). The angle of incidence was 60°. The transmitted fundamental wave was blocked using CuSO₄ solution. A narrow band interference filter centered around 532 nm was used to allow the second harmonic (SH) beam to pass. The SH signal was detected by a photomultiplier tube (PMT), then amplified and averaged in a boxcar integrator (Stanford Research SR-250). Fig.2 shows the experimental set up for SHG measurement.

RESULTS AND DISCUSSION

LB FILM FORMATION

It was extremely difficult to achieve complete vertical transfer of the polymer films onto glass substrates using the Lauda Film Balance. Typically transfer ratios of only 20-30% were achieved on each pass¹⁶. It is believed that this difficulty is due to the extreme rigidity of the polymeric monolayer film. Therefore monolayer characterization and transfer were pursued on the moving wall trough.

Fig.3 shows the pressure-area isotherm of polymers. All the isotherms show similar behavior. For PM5C8MA, the isotherm indicates that the molecules begin to pack into the expanded state at an area of approximately 65 Å per monomer unit. As compression continues, a long

plateau region appears at a relatively low surface pressure. The isotherm then becomes steeper with a limiting molecular area of about 35\AA and collapse occurs at a pressure of approximately 20 mN/m . This behavior suggests that at low surface pressure the polar group (NLO moieties) of polymer side chain are lying flat on the subphase surface, with the hydrocarbon backbone protruding away from the surface. At higher pressure the polar side groups are packed more tightly and are oriented.

However, there is strong repulsion between the polar dipoles in the NLO molecule if they are packed side by side and oriented in the same direction^{17,18}. The LB film was pictured as having an orientation which would be governed by energetically favored packing of the polar groups¹⁰. It is conjectured that the polar groups, for this system, are inclined to the plane of the film at a shallow angle. This permits opposite charges on two polar side groups to find optimal interaction. Monolayer films could be easily transferred onto hydrophilic glass substrates using the vertical deposition method. Transfer ratio of about 1.0 for both upstroke and downstroke was obtained on each pass. The resulting multilayers were Y type. This improvement in transfer is believed to be due to a minimization of shear in the film transfer in the moving wall method.

FILM CHARACTERIZATION

Fig.4 shows the relationship between the peak absorbance from PM5C8MA multilayer at 370 nm and the number of layers in the UV-visible spectra. Good linear relationship was observed. This indicates

that monolayers were stacked up regularly. For the ellipsometry experiment, the sample consisted of multilayers on silicon wafers. From the ellipsometry data it was difficult to get independent accurate measurement of both thickness and refractive index of the ultra thin film. However, good linear relationship was observed between the number of layers and the optical path length (thickness x refractive index) of PM5C8MA multilayer. Assuming the result from the 11 layers sample to be the most reliable, we got 28Å as thickness per layer and 1.635 as refractive index for PM5C8MA.

Polarized UV-visible spectrometry is an effective tool to examine the molecular orientation in LB films^{19,20,21}. Fig. 6 shows the polarized UV-visible spectra at 45° incidence from a multilayer of PM5C8MA. The absorbance of the p-polarized spectrum is week in comparison with the s-polarized spectrum. This result indicates that the NLO moieties are oriented at a shallow angle to the substrate.

ORIENTATION OF NLO MOIETIES

To evaluate the orientation of NLO moieties in the LB film, we consider a dipole model as shown in Fig.7. We assume that the induced molecular dipole moment ($\mathbf{M} = M\mathbf{n}$ where \mathbf{n} is a unit vector) of the NLO moiety is oriented at an angle θ from the normal to the substrate (z axis). The absorbance of such a dipole can be described by²²

$$A = (C / \cos\phi) \operatorname{Im}(\mathbf{M} \cdot \mathbf{E}) / |\mathbf{E}|^2 , \quad (1)$$

where ϕ is the angle of incidence, C is a constant, $\text{Im}()$ represents the imaginary part and $\mathbf{E} = E \cdot \mathbf{e}$ is the incident electric field vector. In the coordinate system shown in Fig.7, the light polarization unit vector \mathbf{e} for s-polarization is $\mathbf{e} = (C, 1, 0)$, (2) and for p-polarization is $\mathbf{e} = (\cos\phi, 0, \sin\phi)$, (3)

The unit vector in the direction of the dipole moment is

$$\mathbf{n} = (\cos\psi \sin\theta, \sin\psi \sin\theta, \cos\theta), \quad (4)$$

where ψ and θ are the orientation angles of the molecular dipole moment (see Fig.7). Using (1)-(4), we get an expression for the absorbance for s-and p-polarization respectively:

$$A_s = (C / \cos\phi) \text{Im}(M) \sin^2\psi \sin^2\theta, \quad (5)$$

$$A_p = (C / \cos\phi) \text{Im}(M) (\cos\phi \cos\psi \sin\theta + \sin\phi \cos\theta)^2. \quad (6)$$

Because there is no preferential orientation in the plane of the substrate, we must average these absorbances over all possible azimuthal angles ψ (from 0 to 2π). After averaging, the expressions (5) and (6) become

$$\langle A_s \rangle = (C / \cos\phi) \text{Im}(M) 1/2 \sin^2\theta, \quad (7)$$

$$\langle A_p \rangle = (C / \cos\phi) \text{Im}(M) (1/2 \cos^2\phi \sin^2\theta + \sin^2\phi \cos^2\theta). \quad (8)$$

Taking the ratio between these two absorbances, we get the expression

$$\langle A_s \rangle / \langle A_p \rangle = \sin^2 \theta / (\cos^2 \phi \sin^2 \theta + 2 \sin^2 \phi \cos^2 \theta). \quad (9)$$

This ratio enables us to calculate the molecular tilt angle θ . For 11 and 5 layers of PM5C8MA and 5 layers of PM2C8MA, the value of θ was estimated to be 60° . From this experiment, we conclude that the NLO moieties (polar groups) in the side chain of all the polymers are lying at an angle of about 30° to the substrate surface. Methylene units are expected to orient away from the substrate surface. Molecular orientation is schematically illustrated in Fig.8.

MIXED MONOLAYER WITH STEARIC ACID

Mixed monolayers of stearic acid and PM5C8MA were prepared in an attempt to optimize the orientation of the NLO moieties in the polymer monolayer. Fig. 9 shows the pressure-area isotherms from monolayers of different component ratios. As a repeat unit, we have taken the average molecular weight of stearic acid and PM5C8MA repeat unit in the appropriate stoichiometry in the mixture. The isotherms of the mixed monolayers show a steeper curve in the high pressure region compared to that of pure PM5C8MA monolayer. Both mixed and pure monolayers show a plateau region. The collapse pressure decreased when the molar ratio of PM5C8MA in stearic acid increased, which suggests a good miscibility of both components.

These mixed monolayers could be easily transferred onto hydrophilic glass substrates using the vertical deposition technique at a

transfer ratio of about 1.0 for both upstroke and downstroke. Fig. 10 shows the polarized UV-visible spectra at 45° incidence from a 5 layer film of a mixture of PM5C8MA and stearic acid (4 : 1). As seen from Fig.10, the θ value did not change significantly and was found to be 65°. Films with other component ratios yield approximately the same θ value.

In the mixed film, the NLO moieties are inclined at a shallower angle to the substrate compared with the pure PM5C8MA multilayer. No improvement in NLO moieties' orientation could be produced even though more stable mixed monolayers could be formed. This is possibly due to the difference in rigidity between the polymer and the stearic acid molecules. Conformational and orientational aspects of the molecular units in the polymer are left unperturbed to a great extent by the incorporation of stearic acid. Stearic acid, however, helps in the overall spreading behavior and surfactive characteristics of the assembly and facilitates the deposition process. Methylene units of stearic acid are probably assembled together with side chains of the polymers to provide the improved stability.

SECOND HARMONIC GENERATION

For the transmitted SH measurements, the samples used consisted of one monolayer deposited on only one side of the glass substrate. Both p-polarized and s-polarized incident fundamental beams generated a p-polarized SH beam (referred to as p-p SH and s-p SH respectively). Although both SH intensities were of the same order of magnitude, the p-p SH beam was stronger than the s-p SH beam. This

confirms that NLO moieties' tilt angle is large as was previously established from UV-visible spectroscopy. No s-polarized SH light was detected. The SH intensity did not change significantly when the sample was rotated around it's normal. This indicates that the film can be modeled as having an in-plane isotropy²³.

We compared the relative p-p SH intensities(I_{SH}) from several samples at an angle of incidence of 60° and found, in order of decreasing SH intensity: PM5C8MA ($I_{SH} = 1$), copolymer-1 ($I_{SH} = 0.51$), copolymer-2 ($I_{SH} = 0.32$), and PM2C8MA ($I_{SH} = 0.29$). According to the polarized UV-visible spectra, PM5C8MA and PM2C8MA have almost the same tilt angle for the NLO moieties. However, the second harmonic intensity of PM5C8MA is larger than that of PM2C8MA. This may be due to better film quality of PM5C8MA as seen in the pressure-area isotherm in Fig.3.

Since there is in-plane isotropy, the SH expression for uniaxial crystals²⁴ can be used. The SH intensities of the samples were compared to the SH intensities of Y cut quartz, ($d_{11}^{(quartz)} = 0.364 \text{ pm/V}$) and yield a d_{33} value of 1.8 pm/V for PM5C8MA. This value is small compared with the d_{33} value of poled copolymer-2 (3pm/V)⁴, in spite of the higher concentration of NLO moieties in the PM5C8MA molecular structure. As described earlier, the NLO moieties have a large tilt angle. The small d_{33} coefficient reflects only the component of the molecular hyperpolarizability tensor perpendicular to the substrate.

Next, we calculate the value of the molecular hyperpolarizability and the tilt angle of the NLO moieties using a different approach²⁵. We assume that the nonlinear component of the molecular dipole moment due to the second order hyperpolarizability β is aligned with the

molecular axis. This axis is at an angle θ (the molecular tilt angle) from the normal of the substrate (Z axis). The molecular hyperpolarizability tensor therefore has only one major component (β), which generates a dipole moment in the direction of the molecular axis^{26,27}. We also assume that the film is isotropic in the plane of the substrate. In the reference frame of Fig. 7, the only non-zero components of the molecular hyperpolarizability tensor, averaged over the azimuthal angle ψ , are therefore of the form^{25,28}

$$\beta_{zzz} = \cos^3 \theta \ \beta , \quad (10)$$

$$\beta_{xxz} = \beta_{yyz} = 1/2 \ \sin^2 \theta \ \cos \theta \ \beta . \quad (11)$$

This molecular hyperpolarizability tensor generates only a p-polarized second harmonic beam, whether the fundamental beam is p- or s-polarized. The second harmonic intensities for the incident s- and p- polarized fundamental beams can be expressed in terms of the molecular hyperpolarizability (β), the molecular tilt angle (θ) and the NLO moieties' surface density(N_s). These relationships are given in the appendix²⁹.

The molecular tilt angle θ is first calculated from the ratio between s-p SH and p-p SH intensities. The NLO moieties' tilt angle was found to be around 55° in PM5C8MA monolayer. This value is in good agreement with the value obtained from polarized UV-visible spectral data. The molecular hyperpolarizability β was computed using the complete expressions for the SH intensities (12) or (13) in the appendix. The molecular surface density N_s is determined from the pressure-area

isotherm ($N_s = 3 \times 10^{15} \text{ cm}^{-2}$ for PM5C8MA). The SH intensities from the monolayer samples were calibrated with respect to the SH intensity of a Y cut quartz plate. For PM5C8MA monolayer, the β value was found to be 1.6×10^{-38} [SI units].

CONCLUSION

LB films of polymers containing NLO moieties in the side chain were characterized by pressure-area isotherm, polarized UV-visible spectroscopy, ellipsometry and SHG techniques. The NLO moieties' tilt angle was calculated from the polarized UV-visible absorbance spectra. The SH intensities generated by polarized fundamental beams were also used to calculate the tilt angle. These results indicate that the NLO moieties in the polymer side chain are lying at an angle of about 30° from the substrate surface. In the mixed monolayers of PM5C8MA and stearic acid, the orientation of the NLO moieties was not improved and the tilt angle remained about the same as in the pure polymer monolayer systems. For PM5C8MA monolayer, the d_{33} value, obtained from the SHG measurements, was 1.8 pm/V , and the β value was 1.6×10^{-38} [SI units].

APPENDIX

For proper estimation of the SH intensity, we must take into account the reflection of both fundamental and SH beams from the substrate. This leads to the following formulae of SH intensities transmitted through the substrate²⁹:

$$I(2\omega)_{s-p} = 8\pi/c \{2\pi k(2\omega)\}^2 N_s^2 \beta^2 I_0(\omega)^2 F_1(\theta, \phi), \quad (12)$$

for s-polarized fundamental beam and

$$I(2\omega)_{p-p} = 8\pi/c \{2\pi k(2\omega)\}^2 N_s^2 \beta^2 I_0(\omega)^2 F_2(\theta, \phi), \quad (13)$$

for p-polarized fundamental beam.

In these expressions c is the velocity of light, $k(2\omega)$ is the magnitude of the wavevector corresponding to the SH beam, N_s is the molecular surface density and $I_0(\omega)$ is the intensity of the fundamental beam. $F_1(\theta, \phi)$ and $F_2(\theta, \phi)$ are angular factors given by:

$$F_1(\theta, \phi) = 1/\cos\phi \{1/4 \sin^4\theta \cos^2\theta \sin^2\phi S^2 t_p(2\omega)^4\}, \quad (14)$$

$$F_2(\theta, \phi) = t_p(2\omega)^4 / \cos\phi \{1/2 G \sin^2\theta \cos^2\phi \cos\theta \sin\phi + L \cos^3\theta \sin^3\phi\}^2, \quad (15)$$

where $t_p(2\omega)$ is the Fresnels' coefficient of transmission through the glass for p-polarized SH light. S, G and L are respectively

$$S = 1 + 2 r_s(\omega) + r_s^2(\omega), \quad (16)$$

$$G = 3 - 4 r_p(\omega) - 2 r_p^2(\omega), \quad (17)$$

$$L = 1 + 2 r_p(\omega) + r_p^2(\omega), \quad (18)$$

where $r_s(\omega)$ and $r_p(\omega)$ are the Fresnels' coefficients of reflection of the fundamental beam from the glass substrate for s-and p-polarizations

respectively. For determination of the NLO moieties' tilt angle (θ), we take the ratio between (12) and (13) which yields

$$I(2\omega)_{s-p} / I(2\omega)_{p-p} = F_1(\theta, \phi) / F_2(\theta, \phi) . \quad (19)$$

For a particular angle of incidence ϕ , this ratio is a single valued function of the tilt angle θ . Expression (12) or (13) may then be used to calculate the value of the molecular hyperpolarizability (β).

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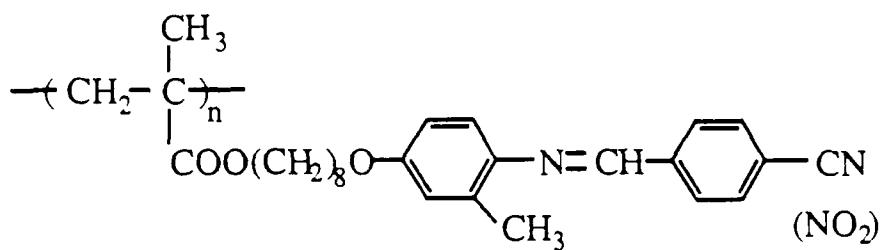
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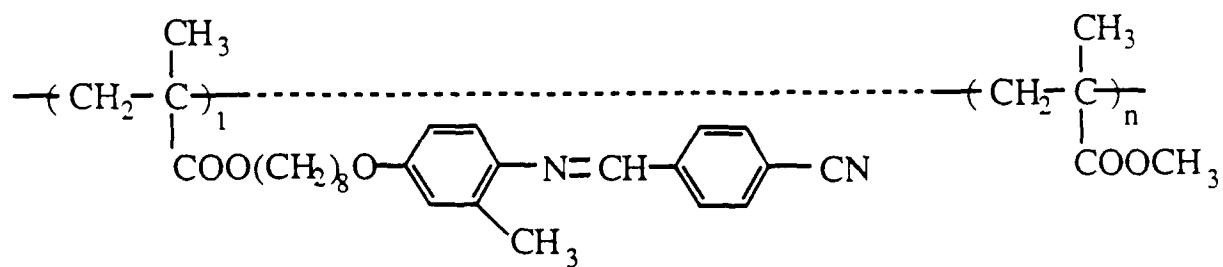
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Legend to the Figures

- Fig.1 Structure of homo- and copolymer.
- Fig.2 Experimental set up for SHG measurement.
- Fig.3 Pressure-area isotherm of polymers on pure water at 20°C, (a) PM2C8MA, (b) PM5C8MA, (c) copolymer-1 and (d) copolymer-2.
- Fig.4 Peak absorbance (370 nm) from PM5C8MA multilayer vs number of layers.
- Fig.5 The optical path length (thickness x refractive index) of PM5C8MA multilayers vs number of layers.
- Fig.6 Polarized UV-visible spectra 11 layers from PM5C8MA (a) p- polarization, (b) s-polarization at 45° incidence.
- Fig.7 Schematic orientation of the molecular dipole and the incident light beam with respect to the substrate surface.
- Fig.8 Schematic illustration of the molecular orientation of PM5C8MA monolayer.
- Fig.9 Pressure-area isotherms of mixed monolayers of PM5C8MA and stearic acid (mole ratio (a) 1 : 1, (b) 4 : 1, (c) 10 :1) on an 2×10^{-4} M CdCl₂ aqueous solution at 20 °C.
- Fig.10 Polarized UV-visible spectra from a 5 layer film of a mixture of PM5C8MA and stearic acid (mole ratio 4 : 1) (a) p- polarization, (b) s-polarization at 45° incidence.



PM5C8MA (PM2C8MA)



copolymer 1 ($n = 2.5$)

copolymer 2 ($n = 9.5$)

Fig. 1 T. Tokuda

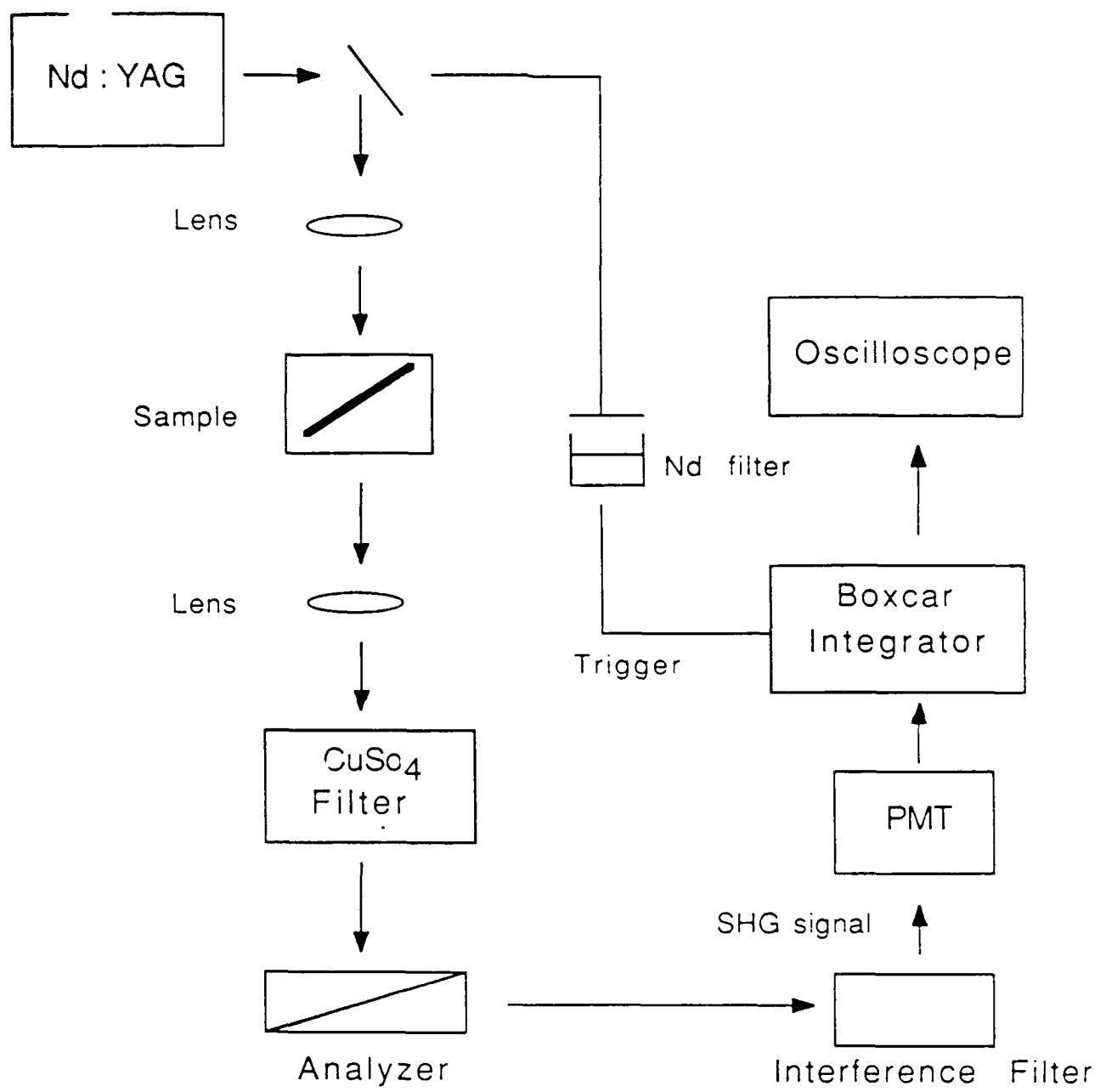


Fig. 2 T. Takahashi

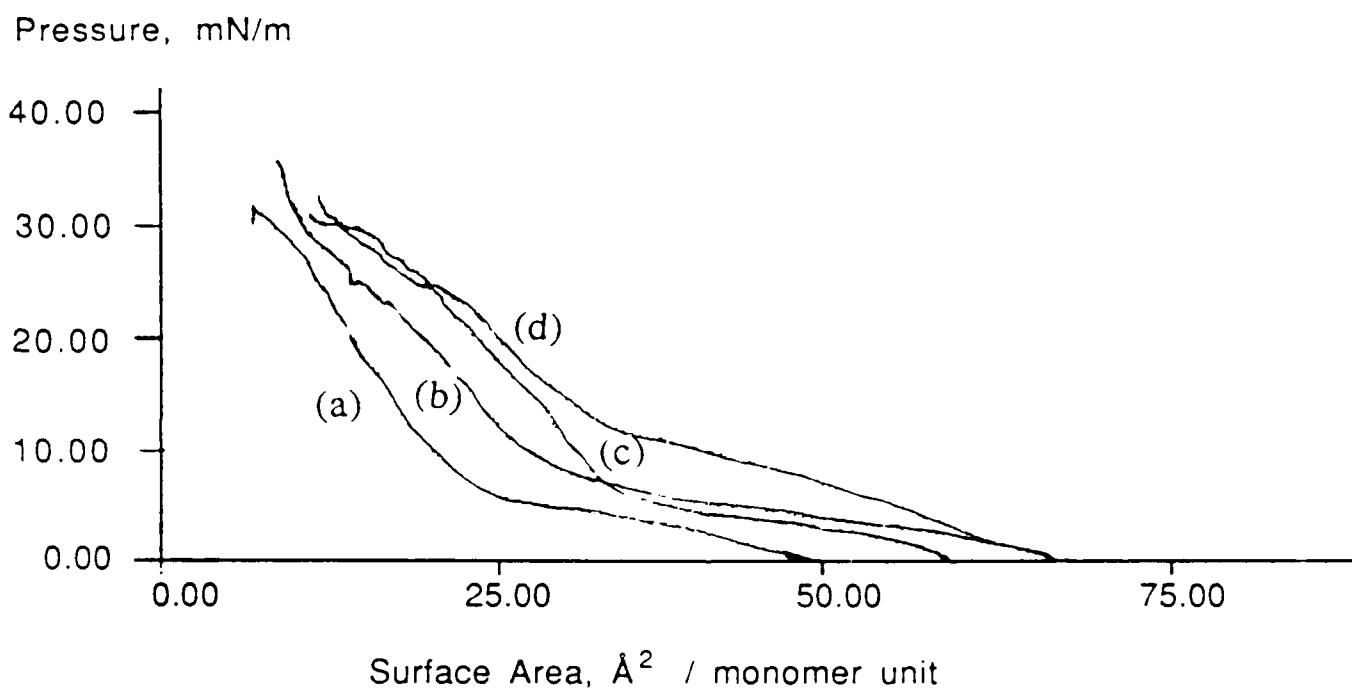


Fig. 3 T. Takahashi

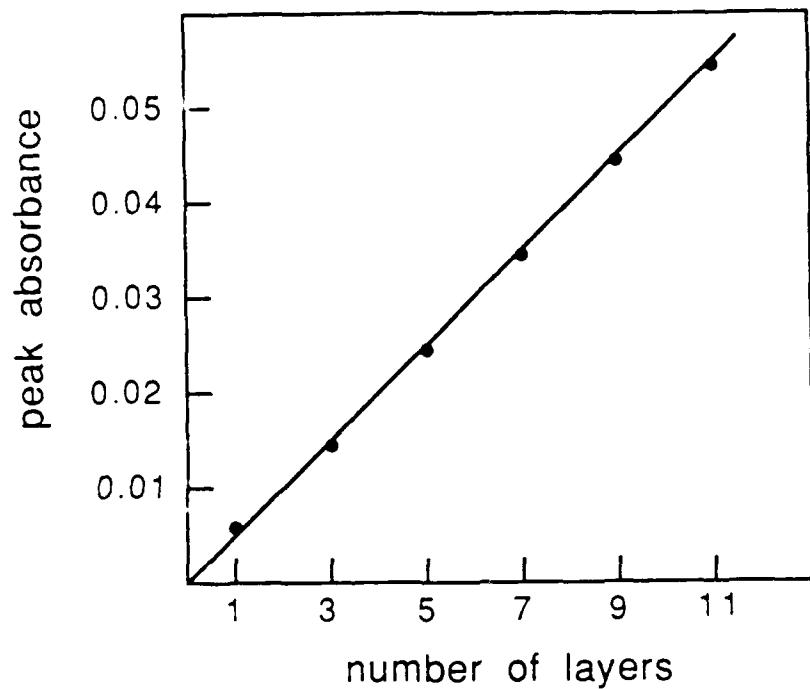


Fig. 4 T. Takahashi

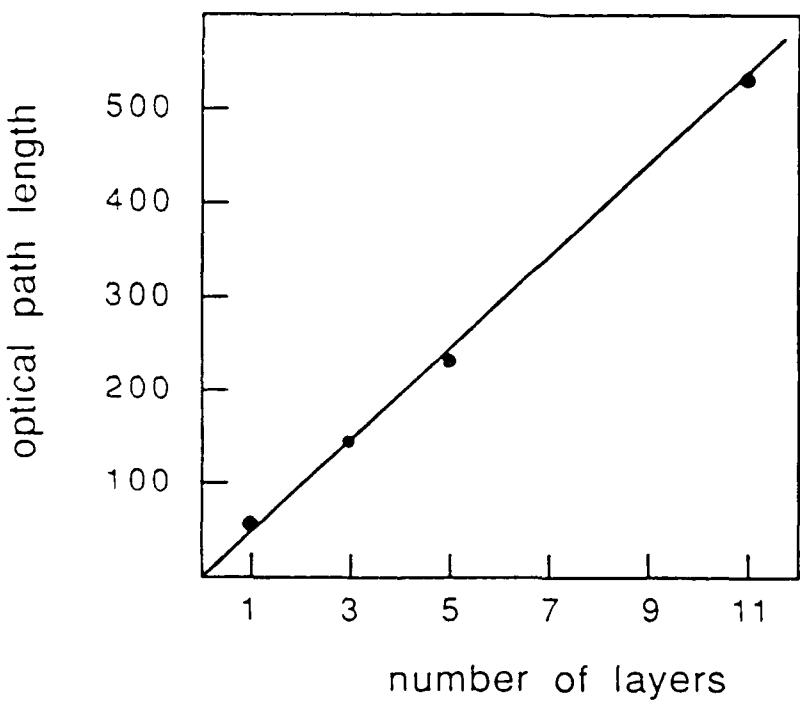


Fig. 5 T. Takahashi

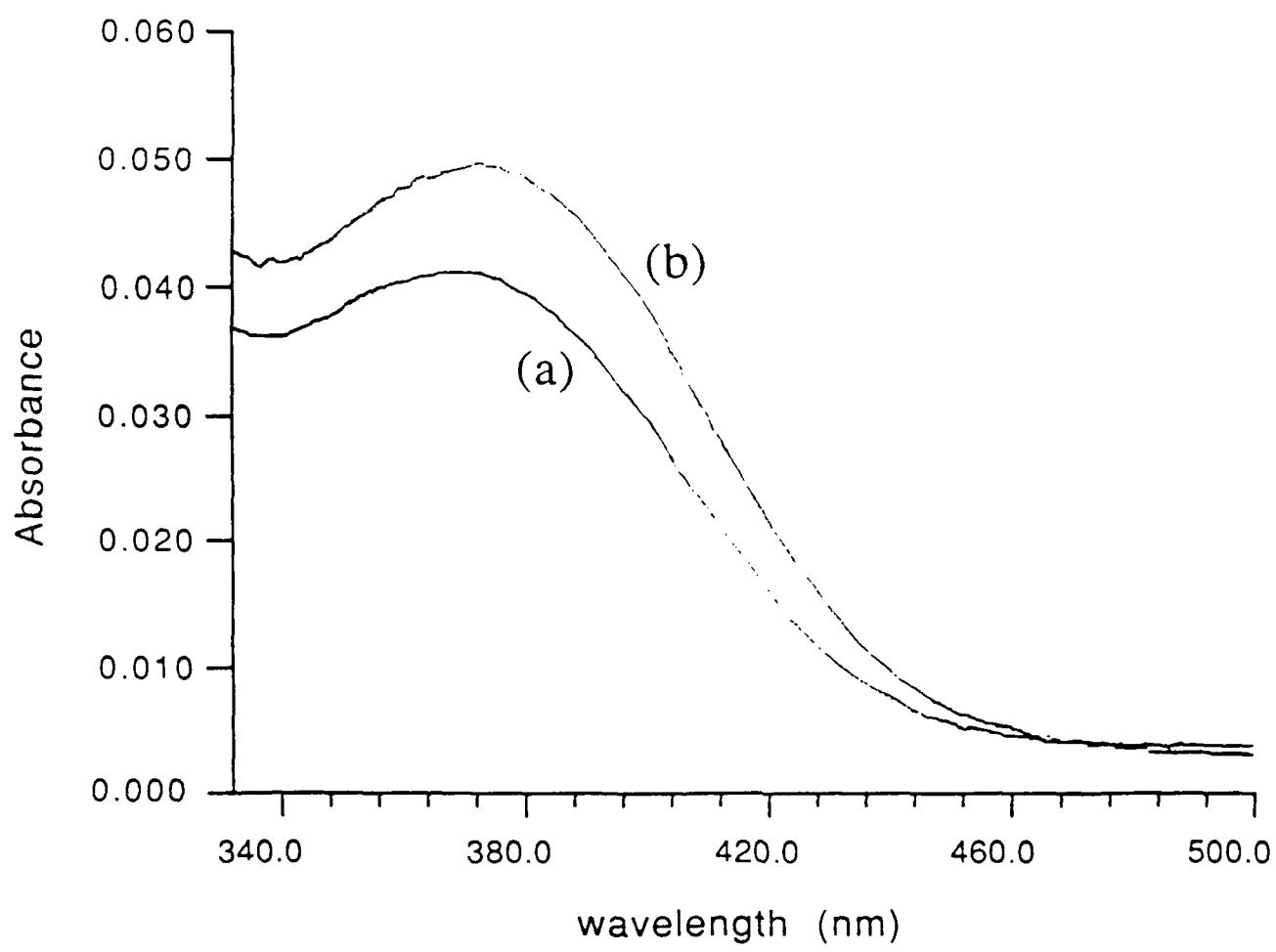


Fig. 6 T. Takahashi

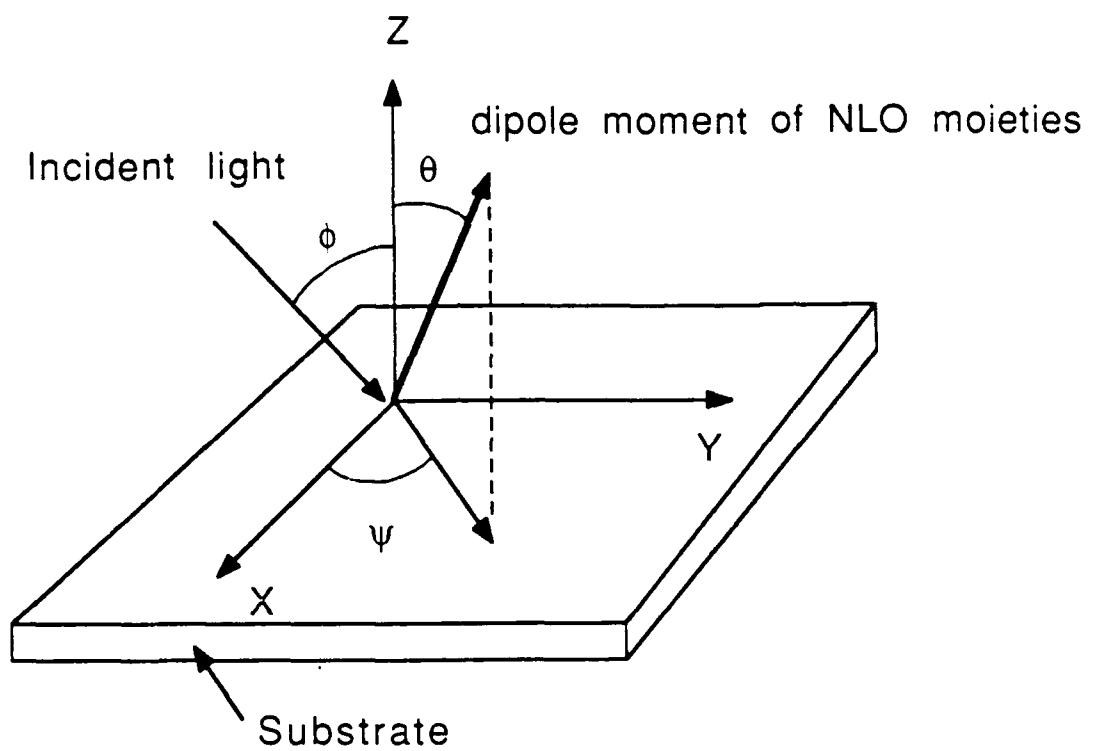


Fig. 7 T. Takahashi

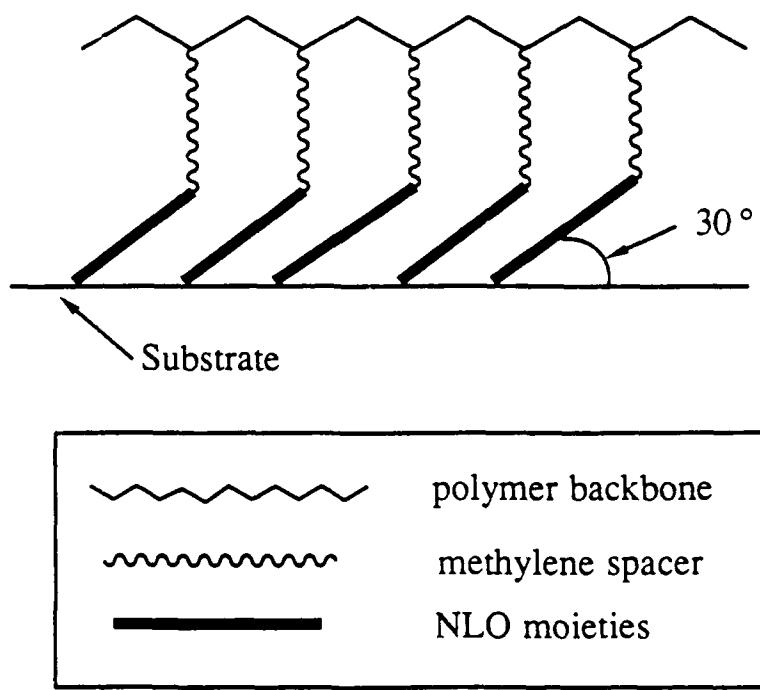


Fig. 8 T. Takahashi

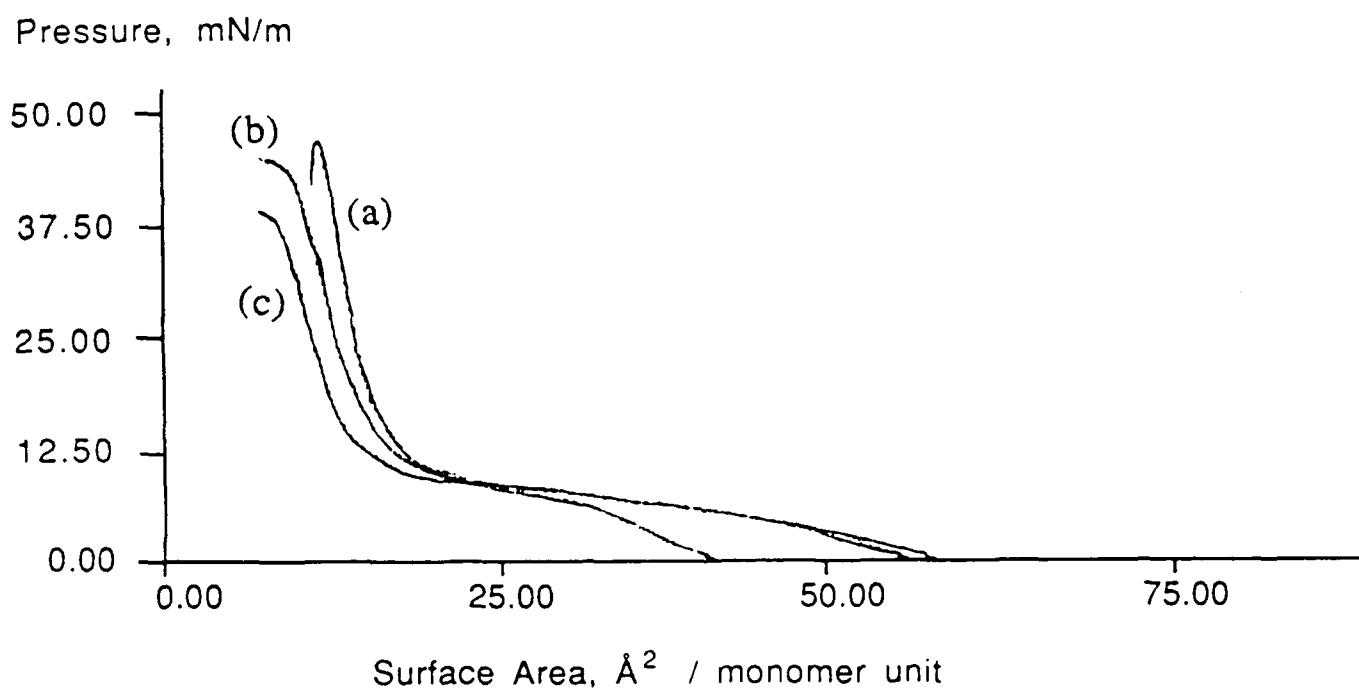


Fig. 9 T. Takahashi:

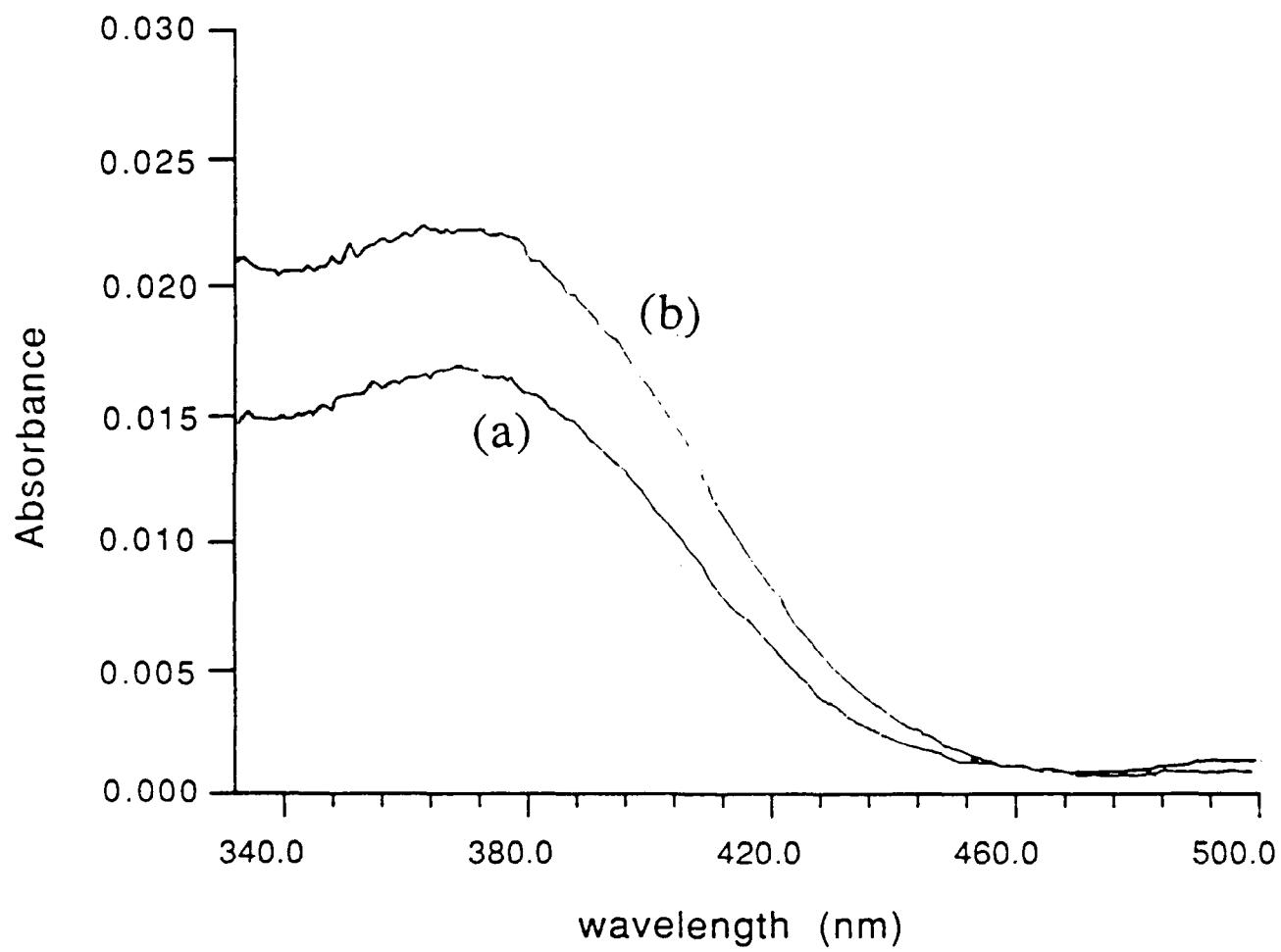


Fig. 10 T. Takahashi;